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Pyrolysis kinetics and physicochemical properties of agropellets produced from spent ground coffee blended with conventional biomass

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ABSTRACT

Spent coffee grounds (SCG), a processing by-product from the coffee industry, were evaluated as a potential feedstock for preparing agropellets for energy production. Hence, pure SCG and a SCG/sawdust blend were transformed into pellets. The latter thermal and chemical properties such as calorific value, ash content, bulk density, fixed carbon and elemental analysis were obtained. Thermogravimetric analyses were conducted in order to determine pyrolysis kinetics and combustion characteristics in order to study the agropellets performance.

The obtained results show that SCG pellets thermal characteristics are in the same order as conventional biomasses such as sawdust. Moreover, blend 50% SCG/50% sawdust reaches the superior NF agropellets standard requirements which are essential to sell this agropellets in the French market. Analysis of the thermal degradation shows that SCG and its blend follow the usual behavior of lignocellulosic materials. Comparison of the combustion characteristics shows a higher reactivity of the blend comparing to pure SCG and sawdust. Such behavior might relate to heterogeneous structure and mutual interaction of the individual components of SCG and sawdust. Pyrolysis kinetics parameters obtained for SCG and SCG/sawdust blend are fairly close agreement with those found in literature for different biomasses. Hence SCG/sawdust may be a promising biofuel for the energy production in industrial applications.

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Keywords: Spent coffee grounds; Agropellets; Thermogravimetric analysis; Pyrolysis kinetics; Combustion characteristics

1. Introduction

The depletion of fossil fuel reserves and the environmental burden from their use have made necessary the use of alternative fuels. Biomass is a clean and renewable energy source leading to environmental, technical and economical benefits. Residues from agricultural production and processing industries are readily available in large quantities. Combustion of these residues can reduce the volume of wastes, allowing for energy recovery and increase of economic returns to rural communities. Coffee is one of the most widely consumed beverages in the world (Mussatto et al., 2011; Nabais et al., 2008a). Spent coffee grounds (SCG), the solid residues obtained from the treatment of coffee powder with hot water to prepare instant coffee, are the main coffee industry residues with a worldwide annual generation of 6 million tons (Tokimoto et al., 2005). SCG are a residue with fine particle size, high humidity (in the range of 80%–85%), organic load, and acidity. SCG are rich in sugars polymerized into cellulose and hemicellulose structures. They are composed by a majority of carbohydrates, being mannose (21.2% w/w), galactose (13.8% w/w) and arabinose (1.7% w/w) from hemicellulose, and glucose (8.6% w/w) from cellulose (Mussatto et al., 2011).

Due to its composition, the use of SCG as an animal feed for ruminants, pigs, chickens, and rabbits have been verified (Claude, 1979; Bressani, 1979). Several studies showed that SCG were suitable as soil conditioner, and organic fertilizer (Bressani, 1979). Moreover, SCG were characterized chemically

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by a high content of carbon source. Hence, SCG were used as biomass precursor for the production of activated carbon using chemical and physical activation (Boonamnuayvitaya et al., 2004, 2005; Nabais et al., 2008b; Boudrahem et al., 2009; Khenniche and Aissani, 2010; Reffas et al., 2010). Several attempts for energy production from SCG have been tested. In particular, Kondamudi et al. have demonstrated that SCG can be used as a potential source to produce biodiesel and fuel pellets, among other value-added products, such as H_2 and ethanol (Kondamudi et al., 2008). Recently, SCG was evaluated as a potential feedstock for preparing biochar fuel (Tsai et al., 2012). Authors have shown that the biochar derived from SCG may be used as a solid fuel in the industrial sector as an alternative for coal (Tsai et al., 2012).

However, the use of raw biomass residue as a fuel often faces several problems, which may limit its wider application for power generation. These include large bulk volume, high moisture content, low heating value and energy density, hygroscopic nature, and smoke during combustion, making it low in combustion efficiency (Deng et al., 2009; Pimchuai et al., 2010). In order to prevent these drawbacks, biomass pelletisation represents a promising solution. In fact, pelletisation increases the specific density of biomass to more than 1000 $kg\,m^{-3}$ (Lehtikangas, 2001; Mani et al., 2004). Pelletized biomass is low and uniform in moisture content. It can be handled and stored cheaply and safely, preventing mold apparition, using well developed handling systems for grains (Fasina and Sokhansanj, 1996). Recently, Limousy et al. have performed combustion tests in domestic pellets boiler using pure SCG and SCG/sawdust agropellets. They have shown that blended pellets (SCG and sawdust) could be a good alternative to pure sawdust. However, the obtained results have indicated that pure SCG are not adapted to residential pellet boilers and further investigation on the thermochemical conversion of SCG are required (Limousy et al., 2013).

Thermogravimetric analysis (TGA) is one of the most commonly used thermal analysis techniques to study the thermal behavior of biomass materials (Jeguirim et al., 2010a; Munir et al., 2009; Dorge et al., 2011; Chouchene et al., 2010a, 2012). Although TGA operates in a different condition compared to a real combustor, it provides an understanding of thermal degradation processes occurring during thermochemical conversion. The aim of the study was to investigate the pyrolysis and the combustion characteristics of pure SCG and its blend with sawdust under TGA conditions. Therefore, ignition temperature, peak thermal degradation temperature and rate and burnout temperature were determined. The obtained data should be useful for further design and operation for energy production system using SCG or its blend as fuels.

2. Materials and methods

2.1. *Samples preparation*

SCG powder, provided by a coffee processing in the east of France (Sotoco, Mulhouse), was transformed into pellets with 6 mm diameter and 15–25 mm length approximately using KAHL 14/175 pelletizer. SCG and pine sawdust were pelletized after being dried and rehydrated to a well-known extent.

2.2. *Samples characterization*

2.2.1. *Proximate and ultimate analysis*

Ultimate analyses corresponding to the elemental compositions of the five samples were carried out by Service Central d'Analyses (Vernaison, France) to determine the weight fraction of carbon, hydrogen, oxygen, nitrogen and sulphur. Proximate analyses were performed using a thermogravimetric analyser (METTLER TOLEDO 851) method described in details in our previous work (Jeguirim et al., 2010a).

2.2.2. *Evaluation of the potential combustion energy*

The high heating values (HHV) were measured using an adiabatic oxygen bomb calorimeter (IKA). The energetic potential of the different biomasses was estimated based on the low heating values (LHV), the bulk density (BD) and the energy density (ED).

2.3. *Thermogravimetric analysis*

Thermogravimetric analyses (TGA) were carried out using a METTLER TOLEDO 851 thermobalance. Initial sample masses of 12 mg were placed in a hemispherical crucible of 4 mm of deep and 9 mm of diameter at its mouth. Experiments were performed under nitrogen or air flows 12 $NL\,h^{-1}$ at 5 $^{\circ}C\,min^{-1}$ from room temperature to 900 °C.

2.4. *Kinetic approach*

A wide range of kinetic schemes have been used for the determination of the apparent activation energy for thermal degradation of lignocellulosic materials including parallel reactions, nucleation models, discrete activation energy models. However, biomass combustion and pyrolysis are complex processes due to differences in the chemical composition of components within the biomass material. Hence, no single kinetic model can explain universally the mechanism of thermal decomposition in all types of biomasses. In the present paper, parameters of the reaction kinetics were determined using the procedure applied by Kumar et al. (2008) and used by many researchers (Jeguirim et al., 2010a; Munir et al., 2009; Dorge et al., 2011; Chouchene et al., 2010a, 2012; Karaosmanoglu et al., 2001; Kumar et al., 2008). Global kinetics of the thermal decomposition can be written as:

$$-\frac{dx}{dt} = kx^n \tag{1}$$

where x is the conversion ratio defined as x: $(w - w_f)/(w_0 - w_f)$ where w_0 is the initial mass at the start of that stage, w_f the final mass at the end of that stage, w the mass at any time, k is the reaction constant and n the order of the reaction.

Applying the Arrhenius equation (2), the combined Eqs. (1) and (2) lead to a linear form Eq. (3) as:

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

$$\ln\left[\frac{-1}{w_0 - w_f}\frac{dw}{dt}\right] = \ln(A) - \left(\frac{E}{RT}\right) + n\ln\left(\frac{w - w_f}{w_0 - w_f}\right) \tag{3}$$

where dw/dt the ratio of change in mass to change in time ($mg\,s^{-1}$), a the preexponential factor (s^{-1}) and R the universal gas constant (8.314 $J\,mol^{-1}\,K^{-1}$), T the absolute temperature (K) and E the apparent activation energy ($J\,mol^{-1}$).

Eq. (3) may be written under the linear form:

$$y = B + Cx + Dz \tag{4}$$

Table 1 – Ultimate analyses of initial sample (daf).

Sample	% C	% H	% O	% N	% S	H/C atomic ratio	O/C atomic ratio
SCG	61.13	8.99	26.60	2.91	0.37	1.765	0.33
Pine sawdust	47.10	6.10	46.27	<0.10	<0.01	1.554	0.74

where $y = \ln\left[\frac{-1}{w_0 - w_f}\frac{dw}{dt}\right]$, $x = \frac{1}{T}$, $z = \ln\left(\frac{w - w_f}{w_0 - w_f}\right)$, $B = \ln(A)$, $C = -\frac{E}{R}$, $D = n$

Constants B, C, D were estimated by multi-linear regression of the TGA data for each stage using Microsoft Excel.

3. Results and discussion

3.1. *Samples characteristics*

Chemical compositions of SCG and pine sawdust as well as the physicochemical properties of the different pellets are summarized in Tables 1 and 2 respectively.

According to Table 1, the weight fractions of the different elements for SCG are in the same order of magnitude than those found for several biomasses in the literature (Jeguirim et al., 2010a; Munir et al., 2009; Dorge et al., 2011; Chouchene et al., 2010a, 2012; Karaosmanoglu et al., 2001; Kumar et al., 2008). Ultimate analysis shows that SCG have a high content of carbon source which demonstrates that SCG can be used as a potential source to produce fuel pellets. Moreover, when placing the SCG in a Van Krevelen type diagram it confirms that SCG is located in the region of typical biomass (Senneca, 2007). However, comparison between the examined biomasses shows a lower O/C atomic ratio for SCG compared to sawdust. Such behavior is attributed to the higher lignin contents in SCG. Previous investigations showed that SCG contains 40% lignin, 37% hemicellulose and 9% of cellulose (Mussatto et al., 2011; Tsai et al., 2012). One may remind that lignin has a lowest O/C atomic ratio close to 0.4 and it is rich in C=C in its aromatic ring as well as methoxyl (–O–CH_3). In contrast, sawdust has a higher O/C atomic ratio due to higher cellulose content. In fact, pine sawdust contains mainly 41% cellulose, 27% hemicellulose and 27% lignin (Saarela et al., 2005). In fact, it is known that cellulose surface is rich in oxygenated groups. The typical functional groups are hydroxyl (–OH) and ether (C—O—C). Table 1 shows that sulfur and nitrogen contents for SCG not allow reaching the NF agro-pellets standard. In particular, SCG has higher nitrogen content (2.91%) comparing to sawdust (<0.10%). Such behavior is attributed to high protein content (13.6%) in SCG comparing to pine sawdust (1.6%) (Mussatto et al., 2011). Hence, it seems necessary to blend SCG with pine sawdust to respect NF agro-pellets and to prevent the generation of hazardous gases.

Table 2 shows the proximate analysis and the energy contents of the densified samples. It is observed that moisture content value is high for SCG pellets. However, it is observed that moisture obtained for the SCG/sawdust blend is approximately twice lower than pure sample. This behavior is attributed to the increase of temperature during the densification process by the friction between the blend of the residues and the complex of die and cylinder of the pelletizer.

Analysis of the volatiles matters and fixed carbon contents shows higher volatiles for sawdust comparing to SCG. This behavior is attributed to higher holocellulose (hemicellulose and cellulose) content in sawdust (68%) comparing to SCG (46%). In fact, it is well known that hemicellulose and cellulose are the main volatiles components. In contrast, the highest fixed carbon is obtained for SCG due to high lignin content which is more stable component. Analysis of energy content values in Table 2 shows that low heating values (LHV) and energetic density are excellent properties for the application of the produced pellets as biofuels. In addition, ash contents are lower than 5% and could reach the NF agropellets. SCG ashes are constituted by several minerals such as potassium (3.5 mg/g), phosphorus (1.5 mg/g), magnesium (1.3 mg/g) and calcium (0.8 mg/g) (Mussatto et al., 2011).

3.2. *Thermal degradation characteristics under inert atmosphere*

In order to determine the thermal characteristics of the different pellet samples, TGA and DTG curves under nitrogen atmosphere are presented in Fig. 1. Moreover, theoretical DTG curve and the corresponding TGA were calculated representing the sum of the individual components behavior in the blend:

$$\left(\frac{dX}{dt}\right)_{blend} = 0.5\left(\frac{dX}{dt}\right)_{SCG} + 0.5\left(\frac{dX}{dt}\right)_{Sawdust}$$

Fig. 1 shows that SCG, sawdust as well as their blend follow the usual shape of lignocellulosic materials. Hence, after moisture release, the thermal degradation under inert atmosphere occurs in two steps. A main devolatilization zone where the thermal degradation rate is higher corresponds to the decomposition of cellulose and hemicellulose and a continuous slight devolatilization zone corresponds to the lignin decomposition and char formation. Comparison between SCG and sawdust thermal degradation shows that devolatilization step occurs earlier for SCG. In fact, during SCG thermal degradation, a small shoulder occurs between 150 °C and 212 °C. The maximum loss rate obtained at 212 °C is 0.0146 wt% s^{-1} (0.175 wt% C^{-1}). This behavior is attributed to the SCG higher lignin content which decomposition started at lower temperature. In fact, Yang et al. showed that lignin decomposed hardly and its weight loss happened in a wide temperature range from 160 to 900 °C (Yang et al., 2006). During the thermal degradation of lignin, the generated solid residue was very high (40 wt%) and occurred at slow rate (0.15 wt% C^{-1}). Above, 212 °C, the SCG mass loss rate increases sharply and peak temperature is reached at 264 °C for a maximum loss

Table 2 – Proximate analysis, high heating value and bulk density of different agropellets.

Sample	Moisture (%)	VM (%)	FC (%)	Ash (%)	LHV (kJ kg^{-1})	BD (kg/m^3)	ED (GJ/m^3)
SCG pellets	11.78	68.94	17.46	1.82	18,110	1211	21.72
Pine pellets	7.90	77.61	14.19	0.30	17,600	1149	20.22
Blend	6.65	78.23	13.94	1.18	18,210	1266	23.05

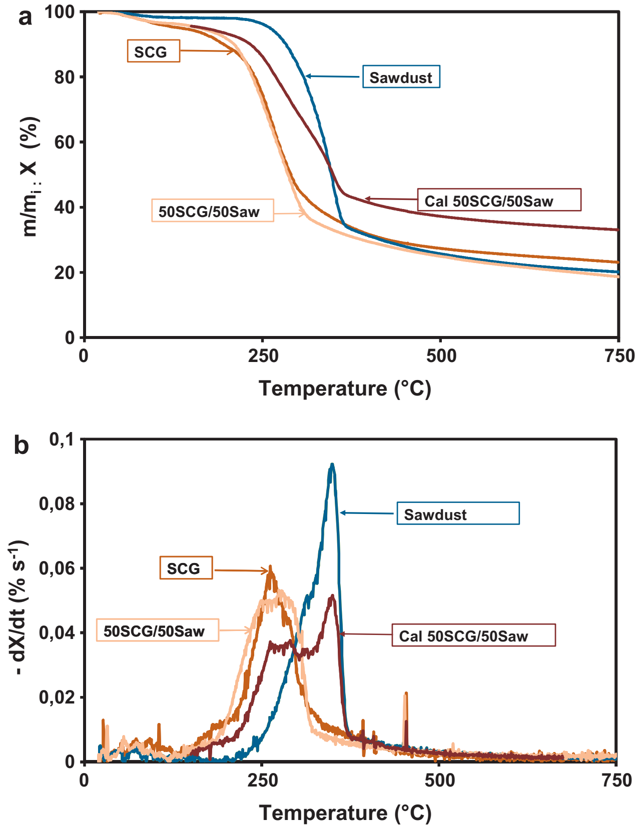

Fig. 1 – TGA (a) and DTG (b) curves of the experiments performed under nitrogen atmosphere.

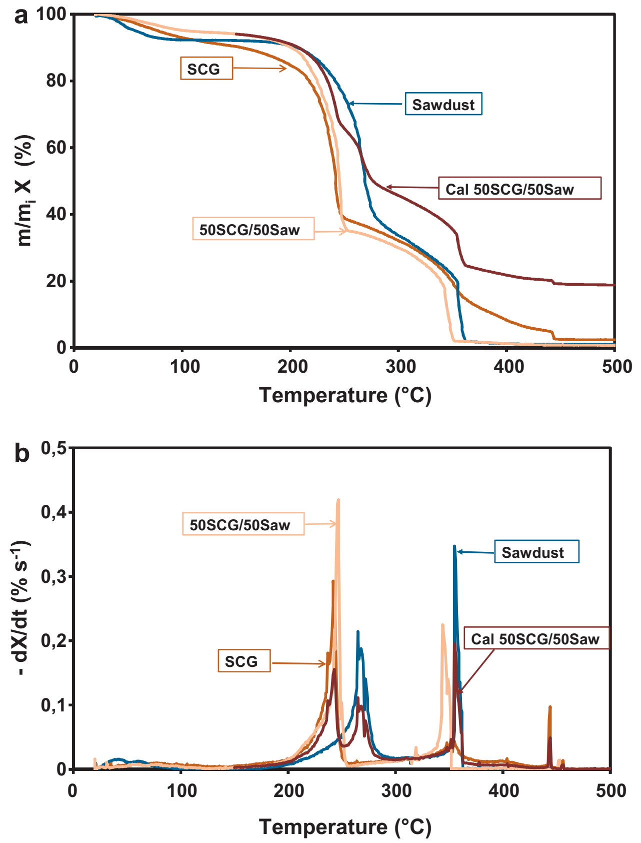

Fig. 2 – TGA (a) and DTG (b) curves of the experiments performed under air atmosphere.

rate of 0.0605 wt% s^{-1} (0.726 wt% C^{-1}). Such peak temperature corresponds to the decomposition of hemicellulose. In fact, Yang et al. showed that hemicellulose decomposed between 220 and 315 °C and got the maximum mass loss rate of 0.95 wt% C^{-1} at 268 °C (Yang et al., 2006). In contrast, sawdust thermal degradation starts at 210 °C and reaches a maximum at 350 °C with a maximum mass loss rate of 0.0923 wt% s^{-1} (1.107 wt% C^{-1}). This behavior corresponds to the thermal degradation of cellulose, which is the main component of sawdust (42%). Yang et al. showed that cellulose pyrolysis occured at a higher temperature range (315–400 °C) with the maximum weight loss rate (2.84 wt%/°C) attained at 355 °C. Orfao et al. obtained a maximum peak temperature of cellulose pyrolysis at 332 °C with a maximum loss rate of 0.98 wt% C^{-1} (Órfão et al., 1999).

The analysis of DTG curve of the SCG/sawdust blend shows that the main devolatilization step is different from the ones obtained for each pure biomass. Hence, during the thermal degradation, the maximum of rate loss is not obtained at a peak temperature but at a large band occurring between 253 and 293 °C. This behavior reveals mutual interactions between components of the blend. This result is confirmed by the comparison between the experimental and the calculated DTG curves of the blend. The higher experimental mass loss rate of the blend than the calculated one and the disappearance of the devolatilization peak of sawdust confirm some interactions between the two biomasses. Hence, the thermal degradation under nitrogen atmosphere cannot be expressed by addition of the individual components of the blend. Such interaction was observed by Yang et al. during the investigation of the thermal degradation of different proportions of hemicellulose, cellulose and lignin under nitrogen atmosphere (Yang et al., 2006).

3.3. *Thermal degradation characteristics under oxidative atmosphere*

Combustion behavior of the different pellet samples was examined. The experimental TGA and DTG curves are shown in Fig. 2. As previously, the calculated TGA and DTG curves for SCG/sawdust blend is presented.

It is evident from the TGA and DTG curves given in Fig. 2 that the three samples demonstrated the usual shape of biomass oxidation curves with three step weight losses; the first accounts for moisture evaporation, the second is due to oxidative devolatilization and the last relates to the combustion of char. Fig. 2 shows as obtained previously under nitrogen atmosphere the devolatilization step occurs earlier for SCG comparing to sawdust. Hence, the first peak of SCG decomposition under air atmosphere is obtained at 242 °C. This peak is attributed to the hemicellulose decomposition. Such shift

Table 3 – Combustion characteristics of the different pellets.

Sample	T_i (°C)	T_b (°C)	T_p (°C)	R (wt% s^{-1})	R_M ($\times 10^3$ wt% C^{-1} s^{-1})
SCG pellets	200	371	242–352	0.293–0.047	1.34
Pine pellets	201	361	265–355	0.214–0.347	1.79
Blend pellets	215	351	247–344	0.419–0.225	2.35

Table 4 – Experimental kinetic parameters during devolatilization step under inert and oxidative atmospheres.

Sample	References	Inert atmosphere				Oxidative atmosphere			
		E (kJ mol^{-1})	ln A (s^{-1})	n	R^2 (%)	E (kJ mol^{-1})	ln A (s^{-1})	n	R^2 (%)
SCG pellets	This work	56.9	6.2	0.50	91	86.2	14.2	0.39	89
Pine pellets	This work	94.4	12.5	0.58	98	105.3	17.7	0.64	98
Blend pellets	This work	62.9	7.6	0.66	95	110.3	19.9	0.32	96
Cotton stalk	Munir et al. (2009)	77.0	–	0.5	98	113	–	0.5	99
Shea meal	Munir et al. (2009)	67.0	–	0.5	81	108	–	0.5	82
Miscanthus pellets	Dorge et al. (2011)	89.0	13	1.02	96	–	–	–	–
Sawdust	Chouchene et al. (2012)	80.6	10.4	0.7	99	107.8	17.4	1	95
Date stone	ElMay et al. (2012)	50.9	4.7	0.71	91	57.7	6.3	0.92	90
Date palm trunk	ElMay et al. (2012)	52.7	4.9	0.46	96	67.6	8.4	0.84	97
Arundo D	Jeguirim et al. (2010b)	–	–	–	–	107.2	–	0.53	99
Miscanthus straw	Jeguirim et al. (2010b)	–	–	–	–	96.4	–	0.59	97
Olive solid waste	Chouchene et al. (2010b)	52.0	4.0	0.61	91	90.	14.0	0.7	91
Wheat straw	Simkovic and Csomorova (2006)	69	–	–	–	111	–	–	–
Bagasse	Nassar et al. (1996)	63	–	–	–	87	–	–	–

to lowest temperature of hemicellulose decomposition under oxidative atmosphere was already observed by Orfaö et al. during the investigation of Xylan thermal degradation (Órfão et al., 1999). Above 260 °C, the rate of char combustion is lower for SCG and occurs in large temperature range with a maximum loss rate at 352 °C. A second sharp peak temperature for SCG combustion is obtained at 444 °C. This peak may be attributed to cellulose char oxidation since Orfaö et al. observed similar second peak at 467 °C during the thermal degradation of pure cellulose under air (Órfão et al., 1999).

Sawdust thermal degradation under oxidative atmosphere exhibits the usual shape of lignocellulosic biomass species oxidation. Hence, a shift to lowest temperature of sawdust devolatilization step under air is observed with peak temperature at 265 °C and a char oxidation step with peak temperature at 355 °C. The difference of SCG and sawdust behaviors may be attributed to a different char structure obtained after the devolatilization step.

The DTG and TGA curves of the SCG/sawdust blend show an interesting result for its future application since the combustion of char occurs earlier comparing to the pure sample. Moreover, as under nitrogen atmosphere, the higher experimental mass loss rate of the blend than the calculated one, the disappearance of the devolatilization peak of sawdust and the obtained char combustion peak temperature confirm mutual interactions between the two biomasses and specially of their components.

Combustion characteristics defined according to Xiang-guo et al. (2006), namely ignition temperature (T_i), peak temperature (T_p), maximal rate loss ($R\%\,s^{-1}$) and burnout temperature (T_b) are shown in Table 3. The mean reactivity ($R_M\%\,C^{-1}\,s^{-1}$) of the different samples based on the method devised by Ghetti et al. (1996) are also shown.

Table 3 shows significant result for the use of the SCG/sawdust blend as promising biofuel. In fact, the mean reactivity of the blend is higher than pure biomasses. This behavior is due to a higher char combustion and a lower combustion temperature range for the blend (SCG 170 °C; sawdust: 160 °C, blend: 135 °C). Such behavior might relate to heterogeneous structure and mutual interaction of the individual components, SCG and sawdust. Moreover, comparison of the obtained values with those found in literature shows that the reactivity of the three samples are higher than those obtained for date palm residues (ElMay et al., 2012) and sugar can bagasse (Munir et al., 2009). However, the main reactivity of SCG pellets is very close to the values obtained by Munir et al. (2009) for cotton stalk and shea meal.

3.4. *Kinetics parameters*

Kinetic parameters such as apparent activation energy, frequency factor and order of reaction for both devolatilization regions under inert and oxidative atmospheres are given in Table 4. The obtained values are compared with those found in literature for other biomasses under similar experimental conditions and using the same kinetics approach.

The values of E calculated during the devolatilization step under inert atmosphere for SCG, pine, and blend pellets were 57, 94, 63 (kJ/mol) and 86, 105, 110 (kJ/mol) under oxidative atmosphere. The analysis of the obtained kinetic parameters confirms the mutual interactions between components of each residue in the blend. In fact, kinetic parameters cannot be expressed by addition of the kinetics parameters of each residue.

The obtained values in Table 4 are quoted to vary with the method and approach used. However, for devolatilization regions in nitrogen and air there is a fairly close agreement with literature data as shown in Table 4. In particular, although apparent activation energy values for SCG cannot be supported by literature since the current study is unique; it is approximated on the grounds of values of other agro-industrial residues such as olive solid waste tested with the same kinetic method (Chouchene et al., 2010b). In addition, Table 4 shows that a change of atmosphere from nitrogen to air resulted in an increase in the values of E. This is also in agreement with the results shown in Table 4.

4. Conclusions

Spent coffee grounds (SCG), a processing by-product from the coffee industry, were evaluated as a potential feedstock for preparing agropellets for energy production. Hence, pure SCG and a SCG/sawdust blend were transformed into pellets. The latter thermal and chemical properties such as calorific value, ash content, bulk density, fixed carbon and elemental analysis were obtained. Thermogravimetric analyses were conducted in order to determine pyrolysis and combustion characteristics in order to study the agropellet performances.

The obtained results show that SCG pellets thermal characteristics are in the same order as conventional biomasses such as sawdust. Moreover, blend 50% SCG/50% sawdust reaches the superior NF agropellets standard requirements which are essential to sell this agropellets in the French market. Analysis of the thermal degradation shows that SCG and its blend follow the usual behavior of lignocellulosic materials. Comparison of the combustion characteristics shows a higher reactivity of the blend comparing to pure SCG and sawdust. Pyrolysis kinetic parameters obtained for SCG and SCG/sawdust blend are fairly in close agreement with those found in literature for different biomasses. Such behavior might relate to heterogeneous structure and mutual interactions of the individual components of SCG and sawdust. Hence SCG/sawdust blend may be a promising biofuel for the energy production in industrial applications.

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